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Authors

Simpson, IJ
Blake, NJ
Blake, DR
[et al.](#)

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Strong evidence for negligible methyl chloroform (CH_3CCl_3) emissions from biomass burning

Isobel J. Simpson,¹ Nicola J. Blake,¹ Donald R. Blake,¹ Simone Meinardi,¹
Mads P. Sulbaek Andersen,¹ and F. Sherwood Rowland¹

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[1] With the phase-out of industrial methyl chloroform (MCF) production, the atmospheric burden of this ozone-depleting gas has rapidly declined. Therefore any non-industrial sources are taking on greater significance in the MCF budget. The only natural MCF source that has been proposed, biomass burning, has been reported to emit up to 2–10 Gg MCF yr⁻¹. We have re-examined MCF data for thousands of airborne and ground-based air samples collected by our group since 1990 that were directly impacted by major biomass burning sources. Without exception, we have found no positive evidence that MCF is released from biomass burning. Our results indicate that global biomass burning emissions of MCF have been significantly overestimated and are unlikely to exceed 0.014 Gg MCF yr⁻¹. Lowering the uncertainty regarding the magnitude of the global MCF biomass burning source may extend its period of usefulness for determining global abundances and trends of the hydroxyl radical (OH). **Citation:** Simpson, I. J., N. J. Blake, D. R. Blake, S. Meinardi, M. P. S. Andersen, and F. S. Rowland (2007), Strong evidence for negligible methyl chloroform (CH_3CCl_3) emissions from biomass burning, *Geophys. Res. Lett.*, 34, L10805, doi:10.1029/2007GL029383.

1. Introduction

[2] Global atmospheric concentration measurements and emission estimates of methyl chloroform (CH_3CCl_3 , MCF) are used to evaluate the global abundance and trends of OH, the most important reactive species in the troposphere [Makide and Rowland, 1981; Montzka et al., 2000; Prinn et al., 2001, 2005]. However, with the phase-out of MCF under the terms of the Montreal Protocol and its amendments, industrial MCF emissions have sharply decreased from a peak of 720 Gg in 1990 to ~20 Gg in 2000 [McCulloch and Midgley, 2001]. Because of its relatively short atmospheric lifetime (~5 years [Montzka et al., 2000; Prinn et al., 2005]), these reduced emissions have resulted in a sharp decrease in the global MCF mixing ratio, from a peak of about 135 pptv in 1992 to 23.3 ± 0.2 pptv in 2004 [Blake, 2005]. Therefore the viability for using MCF to monitor global OH is decreasing as its global mixing ratio becomes increasingly dependent on small emissions [Rudolph et al., 2000], which are harder to accurately quantify. For example the accuracy of the estimated 20 Gg MCF released from industrial sources in 2000, as compared

to field measurements, is being actively debated in the literature [Hurst et al., 2006, and references therein].

[3] In addition to uncertainty regarding its magnitude, the declining anthropogenic MCF source is now approaching the reported magnitude of the only natural MCF source that has been proposed, biomass burning. However, the global biomass burning source of MCF was estimated from a single small study and is therefore also poorly constrained. Using about 20 air samples collected from savanna fire plumes in Ivory Coast, global biomass burning emissions of 4–28 and 16 Gg MCF yr⁻¹ were estimated by Rudolph et al. [1995] and Lobert et al. [1999], respectively. However, because the measurements could have been impacted by sources other than biomass burning and therefore represented an upper limit, the estimate was revised downward to 2–10 Gg yr⁻¹, with the lower end of the range based on laboratory studies in which 7 samples of tropical wood (eucalyptus and musasa) were burned and used as a proxy for all global biomass burning ecosystems [Rudolph et al., 2000]. By comparison, pre-industrial firm air records suggest that natural MCF emissions likely support no more than 2 pptv MCF [Butler et al., 1999; Sturrock et al., 2002], or up to 10 Gg MCF yr⁻¹. Depending on the magnitude of residual anthropogenic emissions, the global MCF mixing ratio could fall below the 2 pptv level by about 2018.

[4] As anthropogenic MCF emissions continue to decline and while alternative methods for OH determination are sought, it is increasingly important to quantify the relative importance of natural MCF sources to the global MCF budget. In addition to ground-based field investigations [Simpson et al., 2002; Wang et al., 2002; Meinardi et al., 2003], our group has collected more than 20,000 air samples since 1990 during a dozen major, international airborne field missions that have focused on or included air sampling in active biomass burning regions on five continents [D. R. Blake et al., 1994; N. J. Blake et al., 1996, 1997, 1999a, 1999b, 2003; Choi et al., 2003; Shirai et al., 2003; Sinha et al., 2003]. Here we present MCF mixing ratios from our most representative biomass burning data sets (i.e. minimally marked by industrial compounds) from the major global source regions, including the burning of: savanna (Africa), savanna and agricultural residues (Brazil), bushfires (Australia), biofuel and crop residues (China), tropical forests (southeast Asia) and boreal forests (Canada). Savanna/grassland fires, biofuel burning, tropical forest fires, extratropical forest fires, agricultural residue burning, and charcoal making/burning are respectively responsible for about 37, 33, 15, 7, 6 and 2% (by mass) of the total dry matter burned globally each year [Andreae and Merlet, 2001; M. O. Andreae, personal communication, 2006]. Ours

¹Department of Chemistry, University of California, Irvine, California, USA.

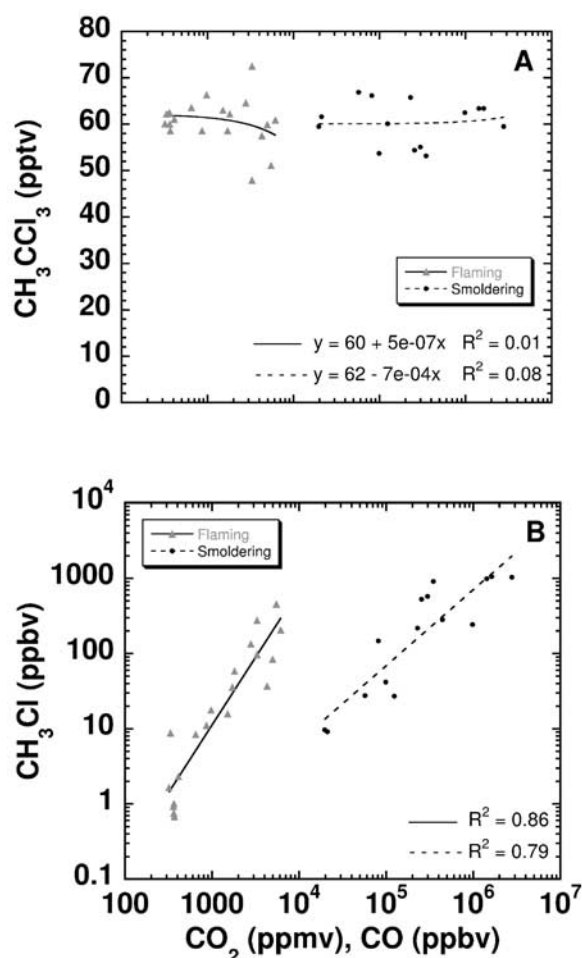


Figure 1. Scatter plots of ground-based air samples heavily impacted by savanna burning in northern Australia, Sep. 1999. (a) MCF vs. CO₂ during the flaming fire stage (triangles, $n = 20$) and vs. CO during smoldering (circles, $n = 14$); (b) CH₃Cl vs. CO₂ during flaming (triangles) and vs. CO during smoldering (circles). The equations displayed in Figure 1a are linear fits to the data. The fits in Figure 1b are linear fits to logarithmic data.

is easily the world's most comprehensive data set describing MCF concentrations in the presence of biomass burning.

2. Experiment

[5] Air samples were collected into conditioned, evacuated 2-L stainless steel canisters each equipped with a bellows valve, usually over a period of about one minute. Pressurized airborne samples were collected using a metal bellows pump, and ground-based samples were collected to ambient pressure by opening the canister valve. The canisters were promptly analyzed at our UC-Irvine laboratory using gas chromatography (GC) with thermal conductivity detection for CO₂, GC with flame ionization detection for CO, GC with electron capture detection (ECD) for MCF from 1990–1998, and GC with ECD and mass spectrometric detection for MCF from 1999 to the present. During TRACE-A (see below) CO was measured using a tunable diode laser (precision = 2%) and CO₂ was measured using a

modified LICOR NDIR analyzer (precision = 0.05%) [see Blake *et al.*, 1996]. The MCF precision has remained at about 1%, the measurement accuracy is 5%, and the detection limit is 1 pptv [Blake *et al.*, 1994; Colman *et al.*, 2001]. The calibration scheme, which is routinely cross-checked against absolute standards from other groups, employs a combination of primary standards prepared from static dilutions of pure MCF, and secondary standards of air collected from different environments and calibrated to certified standards [Colman *et al.*, 2001]. Reactive gases such as O₃, NO, NO₂, and OH have been shown to not survive for longer than a few minutes in our canisters, and in our prior experience with polluted city samples we have not seen evidence for degradation of MCF on particulates.

3. Results and Discussion

[6] Trace gas emissions from biomass burning are often expressed as emission ratios (ERs), i.e. the excess trace gas mixing ratio divided by the excess mixing ratio of a simultaneously measured reference gas, usually CO₂ during a fire's flaming stage ($\Delta\text{CO}/\Delta\text{CO}_2 < 0.1$) and CO during the smoldering stage ($\Delta\text{CO}/\Delta\text{CO}_2 > 0.1$). Our most tightly constrained biomass burning data were collected at ground-level extremely close to active fires (within 3 m) in the Australian savanna (Sep. 1999, $n = 34$). MCF mixing ratios were not elevated in these samples, even though exceptionally high mixing ratios of other emitted species were measured, including the highest levels of dimethyl disulfide (DMDS, 113,000 pptv), dimethyl sulfide (DMS, 34,800 pptv) and methyl nitrate (3,300 pptv) that we have ever detected, compared to typical background values that are roughly 3–4 orders of magnitude lower [Simpson *et al.*, 2002; Meinardi *et al.*, 2003]. These highly concentrated samples led to the discovery that alkyl nitrates are emitted from biomass burning [Simpson *et al.*, 2002]. Therefore, if MCF were emitted from biomass burning, these would be the ideal samples in which to detect it. Instead, even though CH₃Cl ranged over 3 orders of magnitude in these samples (CH₃Cl is primarily emitted during smoldering and is considered one of the more reliable tracer species for biomass burning), the range of MCF was remarkably narrow, with average ($\pm 1\sigma$) MCF mixing ratios during the flaming ($n = 20$) and smoldering ($n = 14$) fire stages of 61 ± 5 and 60 ± 5 pptv, respectively (Figure 1). Even in the sample with the highest levels of DMDS (113,000 pptv) and CO (2,780,000 ppbv) – which were 11,000 and 27,000 times the local background levels, respectively – MCF remained at 59 pptv. Further, MCF showed no correlation with either CO during the smoldering stage or with CO₂ during the flaming stage (Figure 1a and Table 1).

[7] Although our other data sets are not as tightly constrained as the very concentrated Australian samples, they also show no positive evidence that MCF is emitted from biomass burning. Of the ~1500 airborne samples collected during the Sep.–Oct. 1992 TRACE-A experiment, our best encounter with significant regional biomass burning from Africa occurred over Zambian savanna (grasses and small bushes) during flight 10 ($n = 119$) [Blake *et al.*, 1996]. Vertical profiles of MCF and CO during three ascents and three descents clearly show no change in MCF levels within the plumes, which were sampled between 1.5–4.2 km

Table 1. MCF Emission Ratios and Calculated Global MCF Biomass Burning Emissions

Biomass Burning Region and Type	Emission Ratio, pptv/pptv	Number of Samples	Correlation Coefficient	Global Reference Compound Emission, ^a Tg species yr ⁻¹	Calculated Global MCF Emissions, ^b Gg yr ⁻¹
Africa, savanna ($\Delta\text{MCF}/\Delta\text{CO}$)	$(-1.6 \pm 1.1) \times 10^{-6}$	38	$r^2 = 0.06$ $p = 0.16$	690	-5.4 ± 3.7
Africa, savanna ($\Delta\text{MCF}/\Delta\text{CO}_2$)	$(-1.1 \pm 0.8) \times 10^{-7}$	38	$r^2 = 0.05$ $p = 0.17$	13400	-7.0 ± 5.9
Brazil, savanna/crop residue ($\Delta\text{MCF}/\Delta\text{CO}$)	$(-3.9 \pm 2.8) \times 10^{-6}$	30	$r^2 = 0.06$ $p = 0.18$	690	-13 ± 9
Brazil, savanna/crop residue ($\Delta\text{MCF}/\Delta\text{CO}_2$)	$(-1.1 \pm 1.0) \times 10^{-7}$	30	$r^2 = 0.04$ $p = 0.29$	13400	-7.0 ± 6.4
Australia, savanna smoldering ($\Delta\text{MCF}/\Delta\text{CO}$)	$(5.4 \pm 16.6) \times 10^{-10}$	14	$r^2 = 0.01$ $p = 0.75$	690	0.0018 ± 0.0054
Australia, savanna flaming ($\Delta\text{MCF}/\Delta\text{CO}_2$)	$(-7.3 \pm 6.0) \times 10^{-7}$	20	$r^2 = 0.08$ $p = 0.24$	13400	-47 ± 38
Southeast Asia, tropical forest ($\Delta\text{MCF}/\Delta\text{CO}$)	$(-1.3 \pm 1.3) \times 10^{-6}$	39	$r^2 = 0.03$ $p = 0.31$	690	-4.4 ± 4.3

^aAndreae and Merlet [2001].^bBased on the determined ER and the global emission of the reference compound. The uncertainty range is one standard deviation from the regression result.

(Figure 2a). The mean ($\pm 1\sigma$) MCF mixing ratio in the plumes (124.8 ± 1.2 pptv; $n = 29$) was indistinguishable from that for other low-altitude samples (also 1.5–4.2 km) collected outside the plumes (124.7 ± 0.9 pptv; $n = 9$). By contrast, the average CO mixing ratio was 4 times higher inside the plumes (374 ± 118 ppbv) than outside the plumes (88 ± 10 ppbv). Further, these 38 low-altitude MCF samples showed no correlation with CO or CO₂ (Figure 2b and Table 1), whereas CH₃Cl and CO showed excellent correlation and a strong positive slope (Figure 2c).

[8] In addition, small widespread fires associated with field preparation for agriculture were encountered about 800 km NNE of Brasilia, Brazil, during TRACE-A flight 6 at altitudes between 0.6–2.2 km ($n = 101$). As in Africa, the average MCF mixing ratio inside the plumes (125.9 ± 1.6 pptv, $n = 15$) was not significantly different from background boundary layer air (126.9 ± 1.1 pptv, $n = 15$), yet mean CO levels were more than twice as high inside the plumes (291 ± 49 ppbv) compared to background air (124 ± 12 ppbv). Methyl chloroform again was poorly correlated with both CO and CO₂ (Figure 2b and Table 1), whereas CH₃Cl and CO showed excellent correlation and a strong positive slope (Figure 2c). These same African and Brazilian samples have been used to quantify the average emission rates of 16 trace gases from savanna and worldwide biomass burning [Blake *et al.*, 1996]. By contrast, no significant MCF emissions could be established for either continent during savanna burning and the burning of agricultural areas.

[9] Despite their dependence on numerous factors including combustion efficiency and fuel composition, the ERs of CH₃Cl and various nonmethane hydrocarbons (NMHCs) in the Australian, African and Brazilian studies were of the same magnitude (e.g., $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO} = 0.40 \pm 0.09$, 0.59 ± 0.03 and 0.84 ± 0.05 pptv ppbv⁻¹, respectively). Therefore the Australian study is likely to be representative of savanna burning in general [Simpson *et al.*, 2002]. The lack of MCF enhancement in the very concentrated Australian smoke samples gives the clearest evidence to date that MCF is not emitted in significant quantities during savanna burning.

[10] In fact, there is possible evidence from the Australian samples to suggest that some MCF can be destroyed during intense flaming. The five flaming samples with the highest levels of CO₂ showed noticeably lower MCF levels (48–61 pptv) than the remaining samples (59–72 pptv) (Figure 1a). An independent sample *t* test confirmed that the average ERs for both groups are statistically different ($t = 3.2$, $p < 0.01$). We tentatively suggest that MCF may thermally decompose at very high temperature

during biomass burning, though further experiments are needed to confirm this.

[11] In addition to savannas, biofuel burning is a major source of biomass burning emissions (section 1). Based on surface measurements in Oct.–Nov. 1999 at Lin'an, a rural site in eastern China ($n = 12$), enhancements of CO and other gases (e.g. CH₄, CH₃Cl) were consistent with a significant contribution from the burning of biofuels and crop residues [Wang *et al.*, 2002]. However, unlike CH₃Cl and CO, which showed a clear positive slope (1.7 ± 0.3 pptv ppbv⁻¹) and a good correlation ($r^2 = 0.77$, $p < 0.001$), MCF and CO did not correlate ($r^2 = 0.01$, $p = 0.97$, slope = $(-3.9 \pm 11.0) \times 10^{-7}$ pptv pptv⁻¹). The Lin'an results are consistent with those from Brazil, which showed no evidence for MCF emissions from agricultural residue burning. Unfortunately, the large amount of scatter in the data (not shown) renders the magnitude of the slope (ER) very uncertain. Hence, we chose not to consider this dataset further. Although the results give a preliminary indication that biofuels are not a significant source of MCF, a larger number of samples from a wider range of biofuels is encouraged in future work.

[12] During the airborne ABLE-3B experiment in Canada in Jul.–Aug. 1990 ($n = 883$), MCF enhancements were not detected even though a majority of flights encountered some influence from local and/or remote forest fires. For example, the mixing ratio of MCF in a biomass burning plume originating from boreal forests of northwestern Ontario (145.5 ± 0.8 pptv) was not significantly different from the local background value (144.3 ± 2.0 pptv) [Blake *et al.*, 1994]. By contrast, NMHCs were strongly enhanced in this and other plumes (e.g., ethene = 1300 pptv compared to a background of 70 pptv). In addition, the NMHC composition of air recently impacted by fires showed a relatively low variability, which denotes the existence of a typical boreal forest emission signature [Blake *et al.*, 1994]. These findings suggest that North American boreal forest fires are not a significant source of MCF.

[13] Likewise, although the spring 2001 TRACE-P mission was flown over the western Pacific during the peak of the biomass burning season in southeast Asia and India [Heald *et al.*, 2003], we detected no evidence that MCF is emitted from tropical forest fires. Because of the complex mixture of Asian source signatures, samples with a pure biomass burning signature of southeast Asian origin were conservatively selected based on a geographical air mass classification scheme and the criteria CH₃Cl > 625 pptv and the urban air marker CBrClF₂ (H-1211) < 4.35 pptv ($n = 39$)

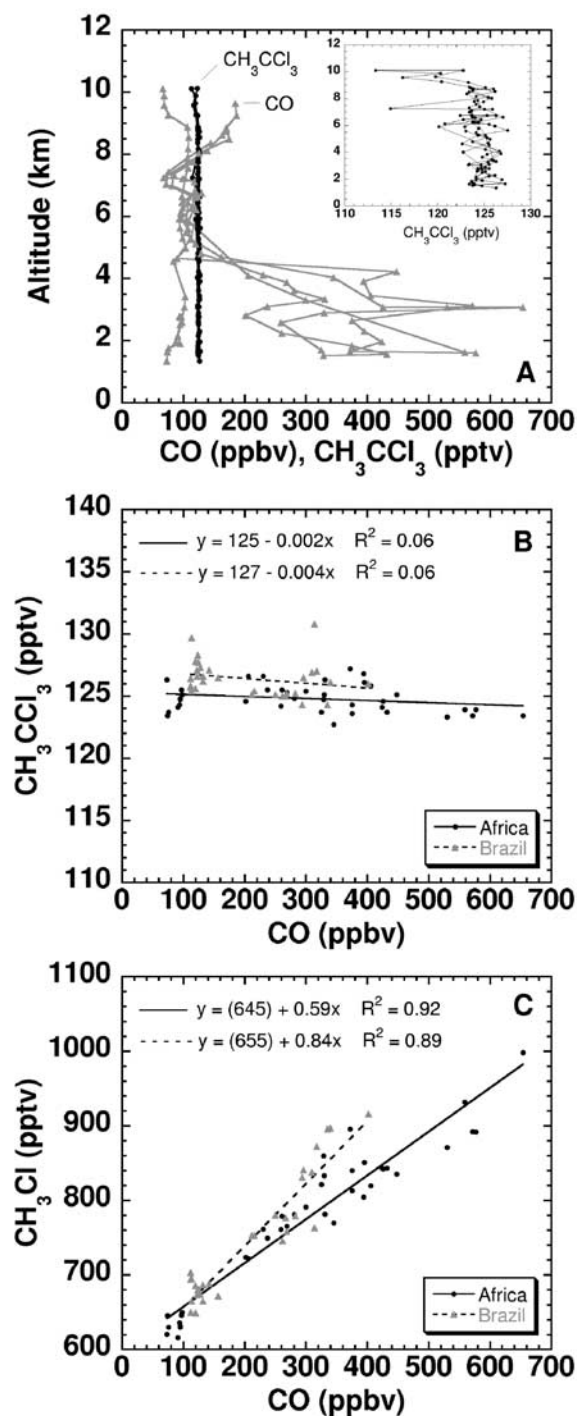


Figure 2. (a) Vertical profiles of MCF (circles) and CO (triangles) in and above air impacted by African savanna burning ($n = 119$) during TRACE-A, Sep.–Oct., 1992. Scatter plots of (b) MCF vs. CO, and (c) CH₃Cl vs. CO in boundary layer air impacted by African (circles, $n = 38$) and Brazilian (triangles, $n = 30$) biomass burning. The displayed equations are linear fits to the data. Because the background mixing ratio of neither CH₃Cl nor CO is zero, a plausible background CH₃Cl value has been substituted for the y-intercept (in parentheses).

[Blake *et al.*, 2003]. These data show no correlation between MCF and CO, and a slope that is not significantly different from zero (Table 1) despite a strong correlation between CH₃Cl and CO ($r^2 = 0.73$, $p < 0.001$; slope = (0.33 ± 0.03) pptv ppbv⁻¹). These results are consistent with a lack of detectable MCF emissions from tropical forest fires.

[14] A lack of MCF enhancements in biomass burning plumes has also been observed during other airborne field missions we have participated in, including the 1995 ACE-1 experiment flown over the South Pacific [Blake *et al.*, 1999a]; the 1996 PEM-Tropics-A experiment, which sampled biomass burning plumes originating from South America and Africa (not shown); the 1999 BIBLE-B mission flown over northern Australia during the late dry season [Choi *et al.*, 2003]; and the SAFARI 2000 mission flown over southern Africa [Sinha *et al.*, 2003]. Further, in contrast to the laboratory results by Rudolph *et al.* [2000], our field measurements do not show evidence that eucalyptus [Shirai *et al.*, 2003] and musasa [Blake *et al.*, 1996] emit MCF.

[15] If global biomass burning emissions of MCF were 2–10 Gg yr⁻¹, as previous work has suggested, then MCF levels of 1740–8470 pptv would have been expected in the Australian smoldering samples, or 30–140 times background levels. At our measurement precision of 1%, the observed MCF value of ~60 pptv in the Australian samples can be measured to within 0.6 pptv, and elevated MCF signals of 1740–8470 pptv would have been easily detected by our analytical system. By contrast, the other data sets had much smaller CO enhancements, and MCF emissions of 10 Gg yr⁻¹ would have given rise to MCF enhancements of 1–3% or 1–2 pptv, with negligible MCF enhancements for emissions of 2 Gg yr⁻¹. These smaller enhancements are much more difficult to detect because they approach the limits governed by the uncertainty of the measurements and the magnitude of the natural variability of background MCF mixing ratios.

[16] We suggest that MCF, CO and CO₂ ranges that are typically measured in biomass burning plumes do not provide sufficient evidence for MCF emissions of 2–10 Gg yr⁻¹ to be clearly excluded [see also Mühle *et al.*, 2007]. Instead, very concentrated samples such as the Australian data are required in order to give ERs and emission estimates that fall well outside the measurement uncertainty. Whereas the MCF vs. CO₂ slope (ER) was negative for the Australian flaming samples (see above), the MCF vs. CO slope was positive for the smoldering samples (Table 1). If we duplicate the calculations of Rudolph *et al.* [2000] and use these smoldering measurements as a proxy for all global biomass burning ecosystems (by scaling the measured ER with the estimated global biomass burning emissions of CO), we obtain a global MCF emission of 0.0018 ± 0.0054 Gg MCF yr⁻¹ (Table 1), as opposed to 2 Gg yr⁻¹. Using a 95% confidence interval, these data give an upper limit of 0.014 Gg MCF released annually from biomass burning.

4. Conclusions

[17] Extensive field measurements spanning more than a decade and collected on five continents show no positive evidence that MCF is released from the world's major

biomass burning sources. Despite strong correlations between CH_3Cl – a good biomass burning tracer – and CO, MCF consistently showed no significant correlation with either CO or CO_2 in air samples impacted by savanna burning, boreal forest fires, tropical forest fires, biofuel burning, or the burning of agricultural residues. We detected no evidence of elevated MCF even in biomass burning samples from Australian savanna fires in which we quantified record-high mixing ratios of other gases, and in which we identified trace gases that had not previously been shown to be emitted from biomass burning. Instead, there is some evidence to suggest that MCF may be destroyed at high temperature during biomass burning. These results give the most compelling evidence to date that biomass burning is not a significant global source of MCF.

[18] Using the most tightly constrained Australian data set as a proxy for all global biomass burning ecosystems – which is supported by results from our other field studies to within their uncertainty ranges – we conservatively estimate an upper limit of 0.014 Gg yr^{-1} (95% confidence interval) for the global biomass burning source of MCF. This value is much lower than the $2\text{--}10 \text{ Gg yr}^{-1}$ reported previously in the literature. A global MCF emission of 0.014 Gg yr^{-1} would support a negligible global MCF mixing ratio of $<0.004 \text{ pptv}$, as compared to an upper limit of 2 pptv suggested by firn air records.

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References

- Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, **15**, 955–966.
- Blake, D. (2005), Methane, nonmethane hydrocarbons, alkyl nitrates, and chlorinated carbon compounds including 3 chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) in whole-air samples, in *Trends: A Compendium of Data on Global Change*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., U. S. Dept. of Energy, Oak Ridge, Tenn.
- Blake, D. R., et al. (1994), Effects of biomass burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands, *J. Geophys. Res.*, **99**, 1699–1719.
- Blake, N. J., et al. (1996), Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region, *J. Geophys. Res.*, **101**, 24,151–24,164.
- Blake, N. J., et al. (1997), Distribution and seasonality of selected hydrocarbons and halocarbons over the western Pacific basin during PEM-West A and PEM-West B, *J. Geophys. Res.*, **102**, 28,315–28,331.
- Blake, N. J., et al. (1999a), Aircraft measurements of latitudinal, vertical, and seasonal variations of NMHC, methyl nitrate, and selected halocarbons during ACE-I, *J. Geophys. Res.*, **104**, 21,803–21,817.
- Blake, N. J., et al. (1999b), Influence of southern hemispheric biomass burning on mid-tropospheric distributions of nonmethane hydrocarbons and selected halocarbons over the remote South Pacific, *J. Geophys. Res.*, **104**, 16,213–16,232.
- Blake, N. J., et al. (2003), NMHCs and halocarbons in Asian continental outflow during the Transport and Chemical Evolution over the Pacific (TRACE-P) Field Campaign: Comparison With PEM-West B, *J. Geophys. Res.*, **108**(D20), 8806, doi:10.1029/2002JD003367.
- Butler, J. H., et al. (1999), A record of atmospheric halocarbons during the twentieth century from polar firn air, *Nature*, **399**, 749–755.
- Choi, Y., S. Elliott, I. J. Simpson, D. R. Blake, J. J. Colman, M. K. Dubey, S. Meinardi, F. S. Rowland, T. Shirai, and F. A. Smith (2003), Survey of whole air data from the second airborne Biomass Burning and Lightning Experiment using principal component analysis, *J. Geophys. Res.*, **108**(D5), 4163, doi:10.1029/2002JD002841.
- Colman, J. J., et al. (2001), Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, **73**, 3723–3731.
- Heald, C. L., D. J. Jacob, P. I. Palmer, M. J. Evans, G. W. Sachse, H. B. Singh, and D. R. Blake (2003), Biomass burning emission inventory with daily resolution: Application to aircraft observations of Asian outflow, *J. Geophys. Res.*, **108**(D21), 8811, doi:10.1029/2002JD003082.
- Hurst, D. F., J. C. Lin, P. A. Romashkin, B. C. Daube, C. Gerbig, D. M. Matross, S. C. Wofsy, B. D. Hall, and J. W. Elkins (2006), Continuing global significance of emissions of Montreal Protocol–restricted halocarbons in the United States and Canada, *J. Geophys. Res.*, **111**, D15302, doi:10.1029/2005JD006785.
- Lobert, J. M., et al. (1999), Global chlorine emissions from biomass burning: Reactive chlorine emissions inventory, *J. Geophys. Res.*, **104**, 8373–8389.
- Makide, Y., and F. S. Rowland (1981), Tropospheric concentrations of methylchloroform in January 1978, and estimates of the atmospheric residence times for hydrohalocarbons, *Proc. Natl. Acad. Sci. U. S. A.*, **78**, 5933–5937.
- McCulloch, A., and P. M. Midgley (2001), A history of methyl chloroform emissions: 1951–2000, *Atmos. Environ.*, **35**, 5311–5319.
- Meinardi, S., I. J. Simpson, N. J. Blake, D. R. Blake, and F. S. Rowland (2003), Dimethyl disulfide (DMS) and dimethyl sulfide (DMS) emissions from biomass burning in Australia, *Geophys. Res. Lett.*, **30**(9), 1454, doi:10.1029/2003GL016967.
- Montzka, S. A., et al. (2000), New observational constraints for atmospheric hydroxyl on global and hemispheric scales, *Science*, **288**, 500–503.
- Mühle, J., T. J. Lueker, Y. Su, B. R. Miller, K. A. Prather, and R. F. Weiss (2007), Trace gas and particulate emissions from the 2003 southern California wildfires, *J. Geophys. Res.*, **112**, D03307, doi:10.1029/2006JD007350.
- Prinn, R. G., et al. (2001), Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science*, **292**, 1882–1888.
- Prinn, R. G., et al. (2005), Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, *Geophys. Res. Lett.*, **32**, L07809, doi:10.1029/2004GL022228.
- Rudolph, J., et al. (1995), Field study of the emissions of methyl chloride and other halocarbons from biomass burning in western Africa, *J. Atmos. Chem.*, **22**, 67–80.
- Rudolph, J., K. von Czapiewski, and R. Koppmann (2000), Emissions of methyl chloroform (MCF) from biomass burning and the tropospheric methyl chloroform budget, *Geophys. Res. Lett.*, **27**, 1887–1890.
- Shirai, T., et al. (2003), Emission estimates of selected volatile organic compounds from tropical savanna burning in northern Australia, *J. Geophys. Res.*, **108**(D3), 8406, doi:10.1029/2001JD000841.
- Simpson, I. J., S. Meinardi, D. R. Blake, N. J. Blake, F. S. Rowland, E. Atlas, and F. Flocke (2002), A biomass burning source of $\text{C}_1\text{--C}_4$ alkyl nitrates, *Geophys. Res. Lett.*, **29**(24), 2168, doi:10.1029/2002GL016290.
- Sinha, P., P. V. Hobbs, R. J. Yokelson, I. T. Bertschi, D. R. Blake, I. J. Simpson, S. Gao, T. W. Kirchstetter, and T. Novakov (2003), Emissions of trace gases and particles from savanna fires in southern Africa, *J. Geophys. Res.*, **108**(D13), 8487, doi:10.1029/2002JD002325.
- Sturrock, G. A., D. M. Etheridge, C. M. Trudinger, P. J. Fraser, and A. M. Smith (2002), Atmospheric histories of halocarbons from analysis of Antarctic firn air: Major Montreal Protocol species, *J. Geophys. Res.*, **107**(D24), 4765, doi:10.1029/2002JD002548.
- Wang, T., T. F. Cheung, Y. S. Li, X. M. Yu, and D. R. Blake (2002), Emission characteristics of CO, NO_x , SO_2 and indications of biomass burning observed at a rural site in eastern China, *J. Geophys. Res.*, **107**(D12), 4157, doi:10.1029/2001JD000724.

M. P. S. Andersen, D. R. Blake, N. J. Blake, S. Meinardi, F. S. Rowland, and I. J. Simpson, Department of Chemistry, University of California, Irvine, Irvine, CA 92697-2025, USA. (isimpson@uci.edu)